# Chemical reactivity of the layered chalcogenide semiconductors WSe$_2$ and InSe controlled by structural and electronic factors

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**Abstract.** The interaction of WSe$_2$ and InSe (0001) van der Waals planes with adsorbed Br$_2$ is investigated by photoelectron spectroscopy (UPS, XPS) and surface photovoltage measurements (SPV) to simulate the active semiconductor/electrolyte interface. Br$_2$ on WSe$_2$ is molecularly adsorbed without any detected surface reaction for all experimental conditions. No surface reaction is obtained on InSe when only UPS measurements are performed. However, a surface reaction of molecularly adsorbed bromine to ionosorbed bromide is induced by x-ray radiation. A strong band bending and SPV effects are observed for the non-reacted interface; for the reacted interface these effects are considerably reduced. The results are interpreted in terms of electronic and structural factors influencing surface reactivity and are related to semiconductor electrochemistry.

## 1. Introduction

The layer-type semiconductors MX$_2$ and MX are characterized by a two-dimensional crystal structure with strong chemical bonding in two-dimensional sandwich-type layers and only weak interaction between the layers [1]. The sandwich-layers are formed by X–M–X or X–M–M–X (X = Se, S or Te, M = metal) repetition units, respectively. Cleaving these crystals leads to similar (0001) surface planes which consist of a hexagonal-close-packed anion lattice with the hexagonally packed metal ions in the trigonal positions of the plane below. Perfect (0001) surfaces are considered to be free of electronic surface states [2]. However, surface states may be formed in photoelectrochemical solar cells by the interaction with the electrolyte, or as intermediates in multi-step corrosion reactions, which may drastically reduce the photovoltage due to strong Fermi level pinning effects [3–5]. In spite of the identical surface structure a very different reaction behaviour has been observed for various layered semiconductors [2]. Evidently chemical and electronic factors, which may be very different [6], considerably affect the surface reactivity.

For this reason we have simulated the semiconductor/electrolyte interface by adsorption of reactive volatile species (preferentially halogens) onto the UHV cleaved surfaces [7–10]. It has been demonstrated that d-band semiconductors (semiconductors with mostly metal d-derived band edge states like MoSe$_2$ [7, 8] do not react with adsorbed halogens. ZrX$_2$ (X = S, Se) (with X p-derived valence band maxima) on

the other hand has been found to be reactive [9]. In this study we have extended our investigations to WSe₂ and InSe. The clean surface and changes due to adsorbed Br₂ are investigated by photoelectron spectroscopy (UPS, XPS) and surface photovoltage measurements (SPV).

## 2. Experimental procedure

The experiments were performed in a commercial UHV multitechnique system (VG ESCALAB MK II) equipped with LEED (VSW) and using He I and Mg Kα as excitation sources. The system and the experimental conditions are described elsewhere in more detail [8]. The crystals were n-type with a typical donor density in the region of $10^{15}$ cm$^{-3}$ for InSe and $10^{17}$ cm$^{-3}$ for WSe₂ [11]. The crystals were mounted with Ag epoxy to ensure reasonable conductivity of the back contact and cleaved in UHV. The adsorption experiments were performed at about 100 K, which means that the sticking coefficient was close to unity. A more detailed description of the experimental procedure is given elsewhere [8].

## 3. Experimental results

For perfectly cleaved surfaces the hexagonal LEED pattern is readily obtained. The UP and XP spectra do not indicate any surface contaminations. The UP valence band features are in agreement with previously published spectra [12, 13, 14]. The photoemission onset of the valence band maximum (difference $E_F - E_{VBM}$) for WSe₂ and InSe is determined to be 1.15 and 1.2 eV, respectively, indicating flat-band conditions.
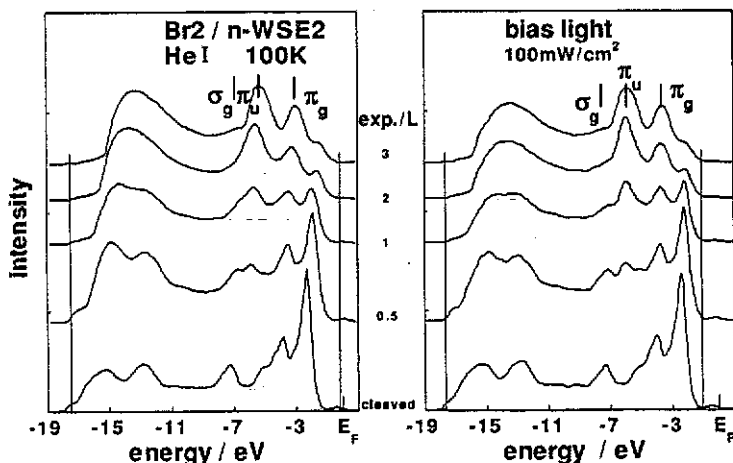


**Figure 1.** He I UP spectra of the n-WSe₂/Br₂ interfaces for increasing Br₂ dosage (a) in the dark (b) in 100 mW cm$^{-2}$ white bias light (the assignment is based on gas phase spectra considering work function and relaxation energy, respectively).

The He I spectra of WSe₂ (0001) in the course of Br₂ adsorption are shown in figure 1 in the dark and under bias light illumination. Due to adsorption of Br₂ extra emission features appear which are assigned to molecularly adsorbed Br₂ [15–18] (as

shown by the lines). In XPS the substrate emission peaks do not show any chemical shifts due to a surface reaction. A small $Br_2$-induced signal appears at $E_B(Br\ 3d) = 70.1\,eV$. From its intensity and considering the weak attenuation of the substrate levels by the absorbate in the He I spectra we conclude that the adsorbed $Br_2$ is deposited in the form of three-dimensional clusters.

The spectral series in the dark (figure 1($a$)) shows a strong shift of the valence band maximum with increasing $Br_2$ coverage due to band bending $(eV_b)$ which is strongly reduced for the illuminated sample (figure 1($b$)) $(eV_b = 0.8\,eV;\ SPV = 0.7\,eV)$. In addition the work function as determined from the secondary-electron onset is drastically increased $(\Delta\phi = 2.2\,eV)$. When the $WSe_2$ sample is annealed at room temperature the molecularly adsorbed $Br_2$ is completely desorbed restoring the spectra to the form obtained for the clean surface.

The He I spectra of the InSe (0001) surface in the course of $Br_2$ adsorption are shown in figure 2 in the dark and under bias light illumination. Similarly to the $WSe_2$-case, adsorption of $Br_2$ leads to extra emission features of molecularly adsorbed $Br_2$ [16–19]. Again a clustering of the adsorbed $Br_2$ is evident.



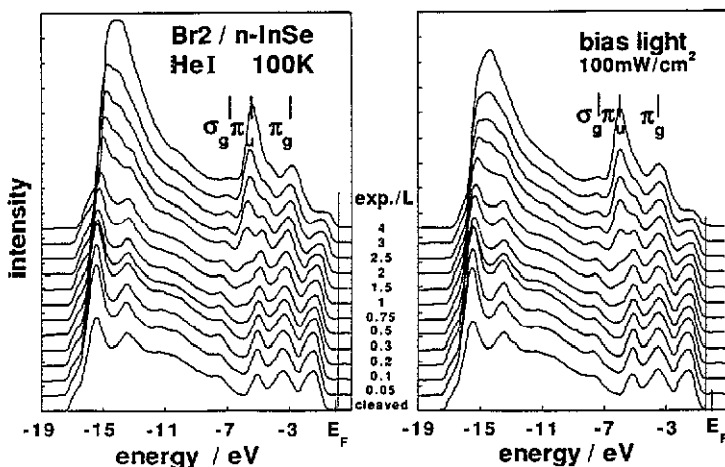**Figure 2.** He I UP spectra of the n-InSe/$Br_2$ interface for increasing $Br_2$ dosage (a) in the dark and (b) in $100\,mW\,cm^{-2}$ white bias light (the assignment is based on gas phase spectra considering work function and relaxation energy, respectively).

As for $WSe_2$ the work function is considerably increased $(\Delta\phi = 1.3\,eV)$. The binding energy shifts due to band bending in the dark $(eV_b = 0.7\,eV)$ and the SPV $(0.6\,eV)$ are also very similar. At $300\,K$ it is possible to remove the adsorbed $Br_2$ completely from the surface when only He I radiation has been used as photoexcitation source.

However, after performing XPS measurements for 30 minutes the spectrum of the molecularly adsorbed $Br_2$ is transformed as shown in figure 3 [11]. The resulting spectral features are assigned to ionosorbed bromide as is evident from comparison of the spectrum to HBr [15] (as given in the figure) and literature spectra of adsorbed halogenides [16–18]. When the sample temperature of the transformed adsorbate is raised to $300\,K$ the ionosorbed $Br^-$ stays on the surface (figure 3, spectrum f).

In the XP spectra of the substrate no additional chemically shifted emission lines could be detected. Also the Mg K$\alpha$ excited In $M_4N_{15}N_{45}$ Auger line does not show
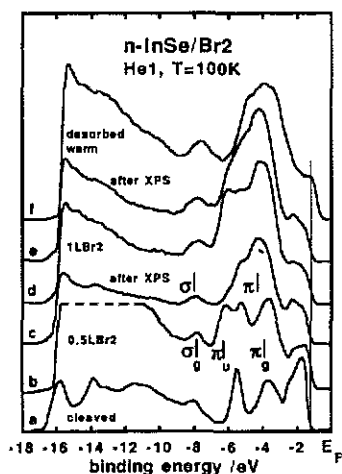
**Figure 3.** He I UP spectra of n-InSe/Br$_2$ interfaces for different conditions: (a) cleaved surfaces at 100 K; (b), (d) after Br$_2$ dosage; (c), (e) after XPS; (f) after annealing at 300 K (the assignment is based on gas phase spectra of Br$_2$ and HBr [18] considering work function and surface relaxation, respectively).

any clear evidence of chemically reacted In. The Br (3d) emission shows up as a very broad feature at 70.05 eV for the adsorbed Br$_2$ at 100 K and at 69.4 eV for the ionosorbed Br$^-$ at 300 K.

Interestingly also the energetic condition of the interface is considerably influenced by the surface reaction. After the x-ray induced surface transformation to ionosorbed Br$^-$ the band bending and the SPV is found to be drastically reduced ($< 0.1$ eV).

## 4. Discussion

Br$_2$ deposited at 100 K onto UHV cleaved (0001) surfaces of WSe$_2$ and InSe is originally molecularly adsorbed in the form of three-dimensional clusters. From the consideration of bulk *thermodynamics* a *reaction* like:

$$2\text{InSe} + 3\text{Br}_2 \rightarrow 2\text{InBr}_3 + 2\text{Se} \tag{1}$$

$$\text{WSe}_2 + 2\text{Br}_2 \rightarrow \text{WBr}_4 + \text{Se} \tag{2}$$

should be highly favourable. The heats of reaction based on tabulated standard heats of formations are [19]:

for reaction (1): $-116$ kcal mol$^{-1}$

for reaction (2): $-32$ kcal mol$^{-1}$

(the calculation is performed for sulphides as the respective values for selenides are not known). For the selenides the possible formation of SeBr$_4$ may add $-17.6$ kcal mol$^{-1}$ per every formed molecular unit. Based on these estimates one should expect that the Br$_2$ molecules react with the surface. However, WSe$_2$ is found to be non-reactive for all our experimental conditions, whereas on InSe the reaction is initiated by an external activation process. The mechanism of x-ray activation has not been definitely identified until now. Since we did not find an activation of the reaction by He I or additional bias light, we tentatively relate it to the capture of secondary electrons by adsorbed Br$_2$ as discussed for O$_2$/GaAs [20]. A process like this has also

been observed for other adsorption systems and has been attributed to a dissociative electron attachment on surfaces [21, 22]. Dissociative adsorption of $Br_2$ demands neighbouring adsorption sites as found on elementary semiconductors and metals. On the layered semiconductors the halogenation of the metal atoms is sterically hindered by the topmost chalcogenide layer. In addition the metal atoms are laterally separated by chalcogene atoms. However, there is a kinetic stabilization effect for $WSe_2$ which cannot be explained by steric factors alone. In spite of similar experimental sequences we do not observe the dissociation of $Br_2$ on the (0001) plane of $WSe_2$ in correspondence to previously published data for $MoSe_2$[7, 8].

The observed difference in reactivity is in addition determined by electronic factors. For the d-band semiconductors (e.g. of group VI B) the electronic interaction with the metal sites is decoupled from the steric interaction which occurs with the topmost chalcogenide layer [9]. The valence and conduction band edges, which are mainly involved in charge transfer interaction with the adsorbate, are derived from metal electron d states. In addition the valence band edge of $WSe_2$, mostly of W $5d_{z^2}$ character, is antibonding with respect to W–Se bonding [23]. Electron transfer from these states to the adsorbate would therefore strengthen the Se–W bonding interaction and stabilize the lattice. On the other hand the valence band maximum of InSe is derived from the bonding $\sigma$ (In $3p_z$) molecular orbital of the In pairs and the Se $4p_z$ levels, which are bonding with respect to In–Se interaction [6, 12]. A charge transfer from these states to $Br_2$ weakens the In–Se bonding and destabilizes the lattice.

Moreover it is interesting to note that band bending and SPV effects are only observed for the non-reacted surface as expected for ideal interfaces between n-type semiconductors and strong electron acceptors like $Br_2$. As soon as a reaction for InSe and thus local bonding of substrate and adsorbate is induced a pinning of the Fermi level close to the conduction band is evident. At the reacted surface electronically active states are formed which do not exist for the cleaved and non-reacted surface. These results indicate that chemical surface reactions determine Fermi level pinning effects at layered semiconductor interfaces. We do not observe any evidence for Fermi level pinning for the $WSe_2$ interface.

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